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Excess isentropic compressibility and computation of sound velocity in ternary liquid mixtures

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Abstract : The values of isentropic compressibility in three ternary systems of acetic acid, propionic acid and butyric acid in aniline-benzene mixture have been evaluated using the measured sound velocities and densities. The deviations from ideality of the K_s values are discussed in terms of structure making effect of the components In addition the validity of Flory's statistical and modified Junjie theory for the computation of sound velocities have been checked out.

Keywords : Carboxylic acid, isentropic compressibility, molecular interaction

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1. Introduction

Excess isentropic compressibility in binary and ternary liquid mixture give an insight in to the structure making and structure breaking effects between the component [1–4]. Molecular interaction in ternary liquid mixture capable of undergoing charge transfer complexation, in terms of excess isentropic compressibilities has been less extensively studied.

In the present investigation the isentropic compressibilities in three ternary systems *viz.*, aniline-benzene-acetic acid (I), aniline-benzene-propionic acid (II) and aniline-benzene-butyric acid (III) have been calculated from the experimental sound velocity and density. Also for these-systems the excess isentropic compressibility has been calculated. Further an attempt

has been made to evaluate the sound velocities in these three systems using Flory's statistical theory [5,6] (FST) and modified Junjie relation [7] (JR). The present work reveals the existence of inter molecular interaction in the systems and the relative merits of the above two theories.

2. Experimental

The chemicals used for the present work were AR grade and purified by the standard method before use. The ultrasonic velocities of the liquid and liquid mixture were measured using pulse-echo overlap method operating at a frequency of 3 MHz at a temperature 303 ± 0.01 K using an electronically controlled thermostat and at a pressure 1 atmosphere. The accuracy of velocity measurements was 2 parts in 10^4. The densities of the mixtures were measured using a specific gravity bottle and the accuracy in the measurements is ± 0.1 kg m^{-3}.

3. Theory

Theoretical sound velocity :

According to Auerbach [8] the sound velocity (U_{FST}), surface tension (σ) and density are related as follows :

$$U_{FST} = \left[\frac{\sigma}{6.3 \times 10^{-4} \times \rho}\right]^{2/3}. \tag{1}$$

The surface tension can be expressed using Flory's [5,6] statistical theory as :

$$\sigma = \sigma^* \sigma(\tilde{v}), \tag{2}$$

where σ^* and $\sigma(\tilde{v})$ are characteristic and reduced surface tensions respectively and these are calculated using the following relations [9] :

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3}, \tag{3}$$

$$\sigma(\tilde{v}) = M(\tilde{v})^{-5/3} - \frac{(\tilde{v})^{1/3} - 1}{(\tilde{v})^2} \ln \frac{(\tilde{v})^{1/3} - 0.5}{(\tilde{v})^{1/3} - 1}, \tag{4}$$

where k is Boltzmann constant, and P^*, T^* and $\tilde{v}$ are the characteristic pressure, temperature and reduced volume, respectively. M is the fraction of nearest neighbours which a molecule loses on moving from bulk of the liquid to the surface. The most suitable value of M has been found to be 0.29 [9] which is used for the present calculations.

The characteristic pressure $\left(P^* = P/\tilde{P}\right)$, temperature $\left(T^* = T/\tilde{T}\right)$ and reduced volume $\tilde{v}$ for the pure liquids are evaluated using the following expressions :

$$P^* = \frac{\alpha T (\tilde{v})^2}{\beta_T}, \tag{5}$$

$$T^* = \frac{T(\tilde{v})^{4/3}}{\left[(\tilde{v})^{1/3} - 1\right]}, \tag{6}$$

and

$$\tilde{v} = \left[\frac{\alpha T}{3(1+\alpha T)} + 1\right]^3, \tag{7}$$

where α and β_T stand for thermal expansion coefficient and isothermal compressibility, and P and T as well as P^* and T^* represent the actual and reduced pressure and temperature respectively. The same quantities for the mixtures are obtained from the equations given below :

$$P^* = \psi_1 P_1^* + \psi_2 P_2^* + \psi_3 P_3^* - \left(\psi_1\theta_2 X_{12} + \psi_2\theta_3 X_{23} + \psi_3\theta_1 X_{31}\right), \tag{8}$$

$$T^* = \frac{P^*}{\frac{\psi_1 P_1^*}{T_1^*} + \frac{\psi_2 P_2^*}{T_2^*} + \frac{\psi_3 P_3^*}{T_3^*}}, \tag{9}$$

and

$$\tilde{v} = \frac{V}{x_1 V_1^* + x_2 V_2^* + x_3 V_3^*}, \tag{10}$$

where ψ refers to segment fraction, θ site fraction and X the interaction parameters of the mixture. The components are indicated by the subscripts 1, 2 and 3 respectively. Assuming the volume reduction parameters of the ternary mixtures to be linear with mole fraction of the component, it is possible to evaluate the characteristic parameters of the ternary mixtures.

The segment and site fractions of the ternary liquid mixtures are calculated using the following relations [6]

$$\psi_3 = \frac{x_3}{x_3 + x_1\left(\frac{V_1^*}{V_3^*}\right) + x_2\left(\frac{V_2^*}{V_3^*}\right)},$$

$$\psi_2 = \frac{x_2}{x_2 + x_3\left(\frac{V_3^*}{V_2^*}\right) + x_1\left(\frac{V_1^*}{V_2^*}\right)}, \tag{11}$$

where $\psi_1 = 1 - \left(\psi_2 + \psi_3\right)$ and

$$\theta_3 = \frac{\psi_3}{\psi_3 + \psi_1\left(\frac{V_3^*}{V_1^*}\right)^{1/3} + \psi_2\left(\frac{V_3^*}{V_2^*}\right)^{1/3}},$$

$$\theta_2 = \frac{\psi_2}{\psi_2 + \psi_3\left(\frac{V_2^*}{V_3^*}\right)^{1/3} + \psi_1\left(\frac{V_2^*}{V_1^*}\right)^{1/3}}, \tag{12}$$

where $\theta_1 = 1 - (\theta_2 + \theta_3)$.

Adopting the familiar Berthelot's relationship

$$n_{ij} = (n_{ii}\, n_{jj})^{1/2}$$

for homopolar species, the interaction parameters have been computed using the following equations :

$$X_{12} = P_1^*\left[1 - \left(\frac{P_2^*}{P_1^*}\right)^{1/2}\left(\frac{S_1}{S_2}\right)^{1/2}\right]^2,$$

$$X_{23} = P_2^*\left[1 - \left(\frac{P_3^*}{P_2^*}\right)^{1/2}\left(\frac{S_2}{S_3}\right)^{1/2}\right]^2$$

and

$$X_{31} = P_3^*\left[1 - \left(\frac{P_1^*}{P_3^*}\right)^{1/2}\left(\frac{S_3}{S_1}\right)^{1/2}\right]^2, \tag{13}$$

where S_1, S_2 and S_3 are the ratio of the molecular surface areas of contact per segment for each species. Thus

$$\frac{S_1}{S_2} = \left(\frac{V_1^*}{V_2^*}\right)^{-1/3}, \quad \frac{S_2}{S_3} = \left(\frac{V_2^*}{V_3^*}\right)^{-1/3} \quad \text{and} \quad \frac{S_3}{S_1} = \left(\frac{V_3^*}{V_1^*}\right)^{-1/3}. \tag{14}$$

Using the above parameters, the ultrasonic velocity in terms of surface tension can be calculated in the light of eq. (1).

The modified Junjie's relation [7] for the calculation of ultrasonic velocity (U_{JR}) in ternary liquid mixtures takes the following form :

$$U_{JR} = \left[\frac{x_1V_1 + x_2V_2 + x_3V_3}{(x_1M_1 + x_2M_2 + x_3M_3)^{1/2}}\right]\left[\frac{x_1V_1}{\rho_1U_1^2} + \frac{x_2V_2}{\rho_2U_2^2} + \frac{x_3V_3}{\rho_3U_3^3}\right]^{1/2}, \tag{15}$$

where x refers to mole fraction, V molar volume, M molecular weight, ρ density and U the velocity of the mixture. The suffixes 1, 2 and 3 represents the mixture components.

Isentropic compressibility :

The isentropic compressibility is obtained from density and velocity as :

$$K_s = U^{-2} \rho_{mi}^{-1} \tag{16}$$

$$\rho_{mix} = \frac{x_1 M_1 + x_2 M_2 + x_3 M_3}{V + V^E} \tag{17}$$

where V^E denote excess molar volume. The excess isentropic compressibility (K_s^E) is given by :

$$K_s^E = K_s - K_s^{id}, \tag{18}$$

where K_s and K_s^{id} denote the isentropic compressibilities of real and ideal mixtures respectively, at the same temperature, pressure and composition. The ideal isentropic compressibility has been computed employing the equation :

$$K_s^{id} = \phi_1 K_{s1} + \phi_2 K_{s2} + \phi_3 K_{s3}, \tag{19}$$

where K_{s1}, K_{s2} and K_{s3} represent the isentropic compressibilities and ϕ_1, ϕ_2 and ϕ_3 the volume fractions of the pure components.

4. Results and discussion

The values of V, U, K_s, the calculated characteristic parameters V^*, T^*, P^* and reduced volume $\tilde{v}$ for each of the pure components are summarised in Table 1. The necessary data to

Table 1. Parameters of pure liquids at 303 K.

Liquid	V $\times 10^6$ $m^3\ mol^{-1}$	U $m\ s^{-1}$	K_s $\times 10^{12}$ m^2N^{-1}	$\tilde{v}$ $\times 10^6$ $m^3\ mol^{-1}$	V^* $\times 10^6$ $m^3\ mol^{-1}$	T^* K	P^* $\times 10^{-10}$ $N\ m^{-2}$
Aniline	91.93	1617.4	377	1.2193	75.3975	5777.19	7.9615
Benzene	90.00	1278.3	705	1.3138	68.5169	4578.54	6.7217
Acetic acid	57.37	1175.0	699	1.2654	45.3372	5081.30	6.0788
Propionic acid	75.54	1199.3	709	1.2694	59.5080	5032.70	6.0004
Butyric acid	93.10	1188.9	748	1.2572	74.0613	5186.03	5.3746

calculate V^*, T^*, P^* and $\tilde{v}$ were taken from literature [10]. Table 2 gives the experimental velocity, density and isentropic compressibility for the three systems along with the percentage deviation of experimental sound velocity from those calculated using FST and JR.

The variation of K_s^E with respect to mole fraction of carboxylic acid is shown in Figure 1. It is observed that the K_s^E values are negative over the entire range of concentration (except at 0.5 mole fraction of acid) in all the three mixtures. The sign and magnitude of K_s^E depends upon two opposing effects namely structure breaking and structure making [11,12].

In all the three systems, the K_s^E increases negatively with addition of carboxylic acid, reaches a maximum value at a critical concentration of 0.2 mole fraction of acid and then tends to

Table 2. Experimental values of density (ρ), velocity (U), isentropic compressibility (K_s) and percentage deviation of sound velocity from experimental velocity at 303 K.

Mole fraction		ρ	U	K_s	Percentage deviation $\Delta U/U$ %	
X_1	X_3	kg m^{-3}	m s^{-1}	$X_2\,10^{12}$ m^2 N^{-1}	JR	FST
			System (I)			
0.4967	0.1023	968 2	1440 4	498	2 81	1 45
0.3990	0.2003	971.9	1399 2	526	2 45	2.28
0.2988	0.3000	975.3	1352.2	561	1 71	3.50
0 2002	0 4014	977.5	1304 0	602	0.82	4 49
0.0980	0.5041	972 5	1234 1	675	1.78	6.32
			System (II)			
0.4972	0 1044	968 9	1439.9	498	2 96	2.02
0.3950	0 2058	971 3	1395 8	528	2 56	3 44
0.2911	0 3053	973.9	1344 3	568	1.47	5 54
0.1954	0 4100	958 7	1293.0	624	0 05	5 77
0.0694	0.5266	953.1	1224 0	700	2 42	8.16
			System (III)			
0 5058	0 1012	968 8	1436.9	500	3.14	2.53
0.3999	0.1979	955.4	1390 0	542	2 83	2 78
0.3008	0.2989	958.0	1344.8	577	2 29	4 71
0.1999	0.4069	940.5	1295.7	633	1 12	4 94
0.1007	0.4975	928.4	1249.0	690	0.05	6.58

become positive, which indicates the existence of strong hydrogen bonding due to the formation of charge transfer complex between aniline and carboxylic acid in benzene. Such a

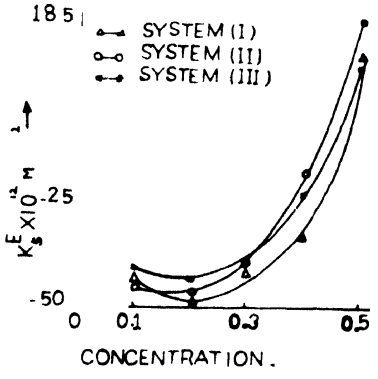

Figure 1. Plot of mole fraction of carboxylic acid *versus* K_s^E at 303 K.

type of interaction between the carboxylic acid and amine in benzene has been confirmed by dielectric [13] and ultrasonic [14] studies. The magnitude of K_s^E for the three mixtures suggests that the strength of interaction is in the following sequence, system(I) > system(II) > system (III).

Thus it is evident from Table 2, Flory's statistical theory provides a satisfactory way of predicting the sound velocity in terms of the surface tension, in spite of the several assumptions and approximations of the theory. A similar observation was noticed in triethylamine with carboxylic acids (acetic, propionic and butyric acids) in benzene mixtures [15].

It is also inferred that (Table 2) the average percentage deviation of sound velocity using JR and FST is 1.90 and 4.30% respectively. This deviations between the observed and calculated sound velocities may be attributed to the molecular association between the carboxylic acids and amine in benzene, which has not been taken into account in the formalism of the above theories. Further, they are inadequate to account comprehensively for the experimental manifestation of molecular interactions in various ultrasonic process.

5. Conclusion

The negative sign of K_s^E is indicative of the structure making effect and its magnitude suggests the presence of strong molecular interaction between the amine and carboxylic acids through charge transfer complex. In addition the present study shows that both the methods give satisfactory results, modified Junjie's relation provide better estimates and predicts excellently the sound velocity in these ternary systems.

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